Raman spectroscopic study of the mineral shattuckite $Cu_5(SiO_3)_4(OH)_2$

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ABSTRACT

Shattuckite $Cu_5(SiO_3)_4(OH)_2$ is a copper hydroxy silicate and is commonly known as a 'healing' mineral. Three shattuckite mineral samples from three different origins were analysed by Raman spectroscopy. Some Raman bands are common in the spectra of the minerals. Raman bands at around 890, 1058 and 1102 are described as the ν_3 $-SiO_3$ antisymmetric stretching vibrations. The Raman band at 670 cm^{-1} is assigned to the ν_4 bending modes of the $-SiO_3$ units and the band at around 785 cm^{-1} is due to Si-O-Si chain stretching mode. Raman (and infrared) spectroscopy proves that water is in the molecular structure of shattuckite; thus the formula is better written as $Cu_5(SiO_3)_4(OH)_2 \cdot xH_2O$.

Keywords: shattuckite, silicate, Raman spectroscopy, hydroxyl ions, planchéite, dioptase

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Introduction

Shattuckite [1, 2] is a copper silicate hydroxide mineral with formula $Cu_5(SiO_3)_4(OH)_2$ [3]. It crystallizes in the orthorhombic - dipyramidal crystal system and usually occurs as well formed prismatic crystals and in a granular massive form and also as fibrous acicular crystals [4-6]. According to Evans and Mrose [4] the structure of shattuckite, $Cu_5(SiO_3)_4(OH)_2$, was refined in the orthorhombic space group Pcab [a = 9.885(1), b = 19.832(2), and c = 5.3825(8) Å; Z = 4 and d. (calcd.) = 4.128. The structure consists of brucite-like (CuO_2) layers with pyroxene-type $(SiO_3)_n$ chains joined to their surfaces.

The two minerals shattuckite and planchéite were first thought to be the same mineral. However it was proven that the minerals were different [7, 8]. Shattuckite is closely allied to planchéite $Cu_8Si_8O_{22}(OH)_4 \cdot H_2O$ in structure and appearance [9]. Shattuckite contains silicate chains similar to pyroxene in a complex association with copper atoms, while the closely related planchéite contains silicate chains similar to amphibole. The mineral is formed as a secondary mineral in oxidized copper deposits. Infrared spectroscopy has been used to differentiate between the copper silicate minerals including chrysocolla, dioptase, shattuckite and planchéite [10] . This differentiation depended upon the presence or absence of the OH stretching vibrations. Some Raman spectroscopic studies of copper silicate minerals mainly chrysocolla has been undertaken in regard to pigments used in ancient and medieval paintings [11]. A data base of minerals used in palettes has been forthcoming [12].

Raman spectroscopy has proven very useful for the study of minerals [13-24]. This paper is a part of systematic studies of vibrational spectra of minerals of secondary origin in the oxide supergene zone. The objective of this research is to report the Raman spectra of shattuckite and to relate the spectra to the molecular structure of the mineral.

EXPERIMENTAL

Minerals

The minerals were supplied by the Mineralogical Research Company. Three mineral samples were used in this study: (a) shattuckite from Bisbee, Cohise County, Arizona (b) shattuckite from Navojoa, State of Sonora, Mexico (c) shattuckite from New Cornelia Mine, Ajo, Pima County, Arizona. Details of the mineral have been published (page 726) [25].

Raman spectroscopy

Crystals of shattuckite were placed on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with 10x, 20x, and 50x objectives. The microscope is part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a CCD detector (1024 pixels). The Raman spectra were excited by a Spectra-Physics model 127 He-Ne laser producing highly polarised light at 633 nm and collected at a nominal resolution of 2 cm^{-1} and a precision of ± 1 cm^{-1} in the range between 200 and 4000 cm^{-1}. Repeated acquisitions on the crystals using the highest magnification (50x) were accumulated to improve the signal to noise ratio of the spectra. Spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer. Previous studies by the authors provide more details of the experimental technique. Alignment of all crystals in a similar orientation has been attempted and achieved. However, differences in intensity may be observed due to minor differences in the crystal orientation.

Infrared spectroscopy

Infrared spectra were obtained using a Nicolet Nexus 870 FTIR spectrometer with a smart endurance single bounce diamond ATR cell. Spectra over the 4000–525 cm^{-1} range were obtained by the co-addition of 128 scans with a resolution of 4 cm^{-1} and a mirror velocity of 0.6329 cm/s. Spectra were co-added to improve the signal to noise ratio. The infrared spectra are given in the supplementary information.

Spectral manipulation such as baseline correction/adjustment and smoothing were performed using the Spectracalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel 'Peakfit' software package that enabled the type of fitting function to be selected and allows specific parameters to be fixed or varied accordingly. Band fitting was done using a Lorentzian-Gaussian cross-product function with the minimum number of component bands used for the fitting process. The Gaussian-Lorentzian ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations of r^2 greater than 0.995.

RESULTS AND DISCUSSION

Background

The isolated tetrahedral SiO_4 unit has 9 internal modes of which four modes are vibrational active due to degeneracy. These vibrations are labelled as ν_1 symmetric stretching mode, the ν_2 doubly degenerate bend, the ν_3 triply degenerate stretching vibration and the ν_4 triply degenerate bending mode. Only the ν_3 and ν_4 modes are infrared active providing the symmetry of the SiO_4 unit is maintained. The values for zircon as an example are ν_1 974, ν_2 266 and 439, ν_3 885, 989 and 1008, and ν_4 430, 608 cm^{-1}. The fact that shattuckite follows a pyroxene type structure means that the siloxane units for polymeric chains and thus the degeneracy of the vibrational modes above will be lifted. The result of this is that the spectra will show much greater complexity. Two types of oxygens may be distinguished namely terminal and bridging oxygens. Additional bands should be observed related to the Si-O-Si bending vibrations.

Raman spectroscopy

The Raman spectra of shattuckite in the 600 to 1400 cm^{-1} region are displayed in Figure 1. Variation in the Raman spectra of the three samples is observed. This may be due to the presence or absence of water in the shattuckite structure (see later). Some bands are common. The band at around 670 cm^{-1} is assigned to the ν_4 bending modes of the -SiO_3 units. Another common band is around 785 cm^{-1}. This band is considered to be a Si-O-Si chain stretching mode. The band at around 980 is attributed to the ν_1 –SiO_3 symmetric stretching vibration. The bands which are approximately in the same position at around 890, 1058 and 1102 are described as the ν_3 –SiO_3 antisymmetric stretching vibrations. Because of the complexity of the spectra it is not possible to assign all the bands in this study. This band is attributed to a SiO_3 stretching vibration of silicate. Dowty [26-28] showed the relationship between crystal structure of silicate minerals and their vibrational spectra. Dowty calculated the band positions for the different ideal silicate units. He showed that the -SiO_3 units had a unique band position of 1025 cm^{-1} [28] (see Figures 2 and 4 of this reference). Crystalline and amorphous SiO_2 does not show any bands in this position [28].

The fact that shattuckite follows a pyroxene type structure means that the siloxane units for polymeric chains and thus the degeneracy of the vibrational modes above will be lifted. The result of this is that the spectra will show much greater complexity. Two types of oxygens may be distinguished, namely terminal and bridging oxygens. Additional bands should be observed related to the Si-O-Si bending vibrations. The Raman spectrum of shattuckite displays a band at 1043 cm^{-1} with a shoulder band at 1048 cm^{-1}. Dowty's calculations predicted the band at 1081 cm^{-1} is attributable to a Si_2O_5 silicate unit [28]. The 1043 cm^{-1} band of shattuckite is in a similar position to the 1042 cm^{-1} of chrysocolla.

The infrared spectrum of the three shattuckite mineral samples is displayed in Figure S1. The spectra appear complex with many overlapping bands which may be resolved into component bands as shown. The infrared bands in the 1000 to 1200 cm^{-1} are assigned to the ν_3 $-SiO_3$ antisymmetric stretching vibrations. These bands are more intense in the infrared spectra compared with the Raman spectra. The band at 998 cm^{-1} (953 cm^{-1} for sample b, 964 cm^{-1} for sample c) is possibly the ν_1 $-SiO_3$ symmetric stretching vibration. The low intensity infrared bands at around 668 cm^{-1} is assigned to the ν_4 bending modes. Again it is not possible to attribute all of the bands.

The Raman spectra of shattuckite in the 100 to 600 cm^{-1} region are shown in Figure 2. The Raman bands at around 395 and 441 cm^{-1} are attributed to the ν_2 bending modes. Another possibility because of the removal of degeneracy, the bands could be attributed to the ν_4 bending modes. The Raman spectrum of sample (a) resembles that of (b) in this spectral region. But spectrum of (c) is different. It is thought that this difference rests with the presence or absence of water in the molecular structure of shattuckite. Samples (a) and (b) appear to contain water where as water is absent in sample (c). The strong Raman band at 216 cm^{-1} (sample a) and 211 cm^{-1} (sample b) is thought to be associated with hydrogen bonding in the molecular structure of shattuckite. The band is absent or of significantly lower intensity in the spectrum of sample (c). An intense sharp Raman band is observed at 699 cm^{-1} for planchéite. A very intense sharp Raman band is found for shattuckite at 670 cm^{-1}. Dowty [28] predicted a Raman band for -SiO_3 units at around 650 cm^{-1}. Dowty calculated the position of this band for not only SiO_3 units but also for Si_4O_{11} and Si_2O_5 units. The band is in the same position for these units. This is explainable when the assignment of this band is to the ν_4 bending modes.

The Raman spectrum of shattuckite in the 2600 to 3800 cm^{-1} region is displayed in Figure 3. The intense sharp band at around 3604 cm^{-1} for sample (a) is assigned to the OH stretching vibration of the OH units in the shattuckite structure. Additional low intensity bands are found at 2913, 3053, 3179 and 3353 cm^{-1}. These bands are attributed to water stretching vibrations. The range of wavenumbers indicates that the water is involved in a range of hydrogen bonding. Because of the nature of the structure of shattuckite in a pyroxene structure the water molecules are bonded to the OH units. A similar spectrum is found for sample (b) from Navojo, Mexico. Here the intense band is observed at 3602 cm^{-1} and component bands are observed at 3153, 3367, 3424 cm^{-1}. The assignment of the bands is as before. For sample (c) the intense Raman band is observed at 3617 cm^{-1} with shoulders at 3584 and 3611 cm^{-1}.

The infrared spectra of the OH stretching region are reported in Figure S2. For sample (a) strong sharp bands are observed at 3604 and 3629 cm^{-1}; for sample b the band attributable to the OH stretching wavenumber is observed at 3606 cm^{-1}; this band is observed at 3627 cm^{-1} for sample (c). The intensity of bands ascribed to water stretching vibrations show a much greater intensity in the infrared spectrum. For sample (a) infrared bands are observed at 2959, 3265, 3335, 3461 and 3577 cm^{-1}; for sample (b) infrared bands are found at 2865, 3208, 3360 and 3522 cm^{-1}; and for sample (c) an intense bands is observed at 3213 cm^{-1}. The position of these bands show that water is involved in differing hydrogen bond strengths. The infrared spectra appear to be different for each of the shattuckite minerals.

The Raman and infrared spectra of shattuckite in the 1400 to 1800 cm^{-1} region are displayed in Figures 4 and S3 respectively. The spectrum of sample a shows two bands at 1545 and 1606 cm^{-1}. This latter band may be due to a water bending vibration. For sample (b) a broad low intensity Raman band is observed at 1564 cm^{-1}. It is thought that bands in this position may be attributable to OH deformation mode. The band is observed at 1561 cm^{-1} for sample (c) with a shoulder at 1488 cm^{-1}. The infrared spectrum displays a low intensity band at 1626 cm^{-1} (a) and 1619 cm^{-1} (b). These bands are attributed to water bending modes. It is interesting that no band was observed for sample (c), indicating no water was adsorbed on the shattuckite surface. The Raman and infrared spectra clearly show that water is strongly hydrogen bonded in the structure of shattuckite. Thus the formula of shattuckite might not be

193 written as $Cu_5(SiO_3)_4(OH)_2$ but may be better written as $Cu_5(SiO_3)_4(OH)_2 \cdot xH_2O$. This
194 formula is exemplified by the samples (a) and (b). The following reaction is envisaged to
195 represent the uptake of water:

196 $$Cu_5(SiO_3)_4(OH)_2 + xH_2O \rightarrow Cu_5(SiO_3)_4(OH)_2 \cdot xH_2O$$

197

198 **CONCLUSIONS**

199 The mineral shattuckite is a copper hydroxy silicate $Cu_5(SiO_3)_4(OH)_2$. Based upon the
200 vibrational spectroscopy of the hydroxyl stretching region, OH units are involved in very
201 strong hydrogen bonding in shattuckite and there is evidence that water is involved in the
202 structure of the mineral. It is proposed that the formula may be better written as
203 $Cu_5(SiO_3)_4(OH)_2 \cdot xH_2O$.

204

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List of Figures

Figure 1 Raman spectra of shattuckite from (a) Bisbee (b) Navojoa (c) Ajo in the 600 to 1400 cm^{-1} region.

Figure 2 Raman spectra of shattuckite from (a) Bisbee (b) Navojoa (c) Ajo in the 100 to 600 cm^{-1} region.

Figure 3 Raman spectra of shattuckite from (a) Bisbee (b) Navojoa (c) Ajo in the 2600 to 3800 cm^{-1} region.

Figure 4 Raman spectra of shattuckite from (a) Bisbee (b) Navojoa (c) Ajo in the 1400 to 1800 cm^{-1} region.

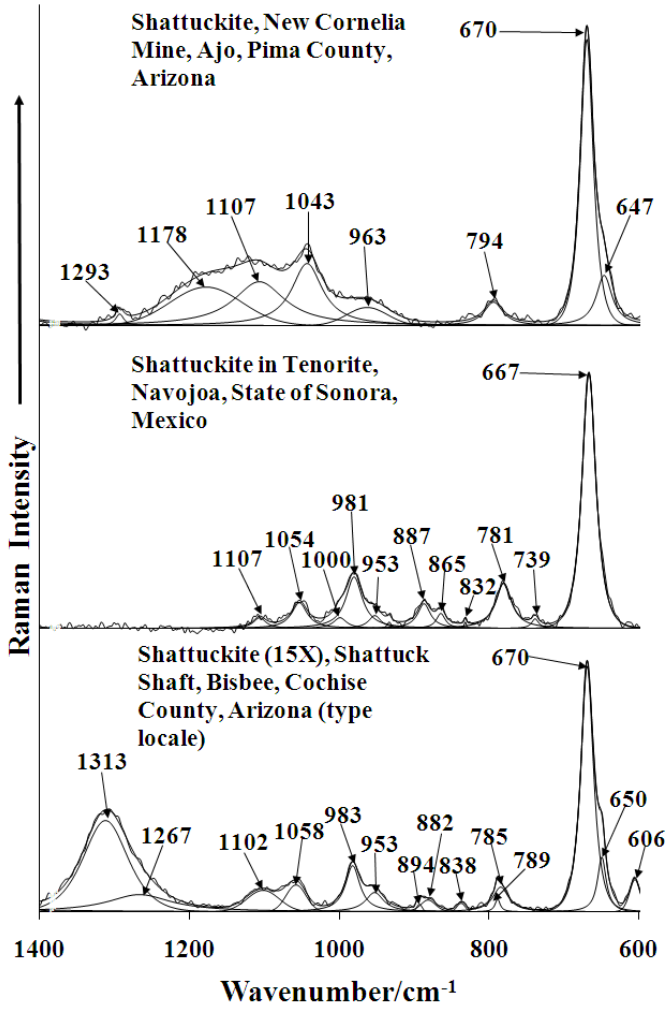
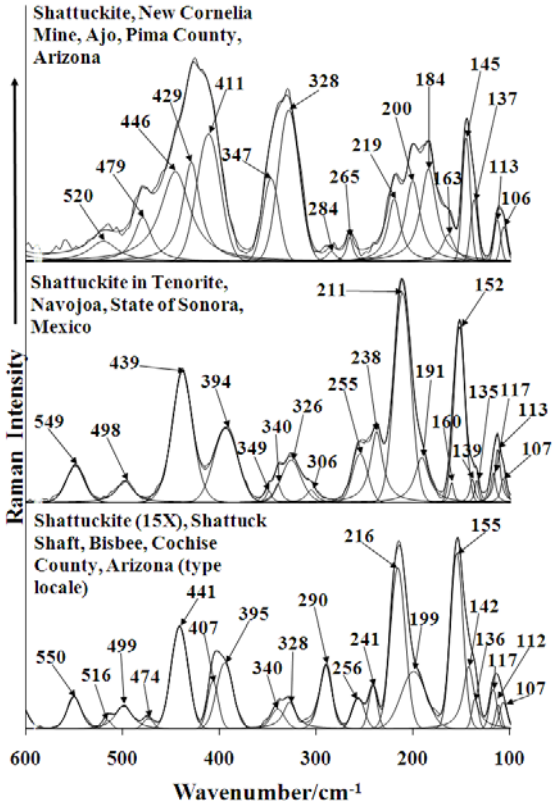

Shattuckite, New Cornelia Mine, Ajo, Pima County, Arizona
670
647
1107
1043
1178
963
794
1293
Shattuckite in Tenorite, Navojoa, State of Sonora, Mexico
667
981
1054
887
781
1107
1000
953
865
739
832
Shattuckite (15X), Shattuck Shaft, Bisbee, Cochise County, Arizona (type locale)
670
1313
650
983
882
1267
1102
1058
953
785
606
894
838
789
Raman Intensity
1400
1200
1000
800
600
Wavenumber/cm-1

Figure 1



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274 **Figure 2**

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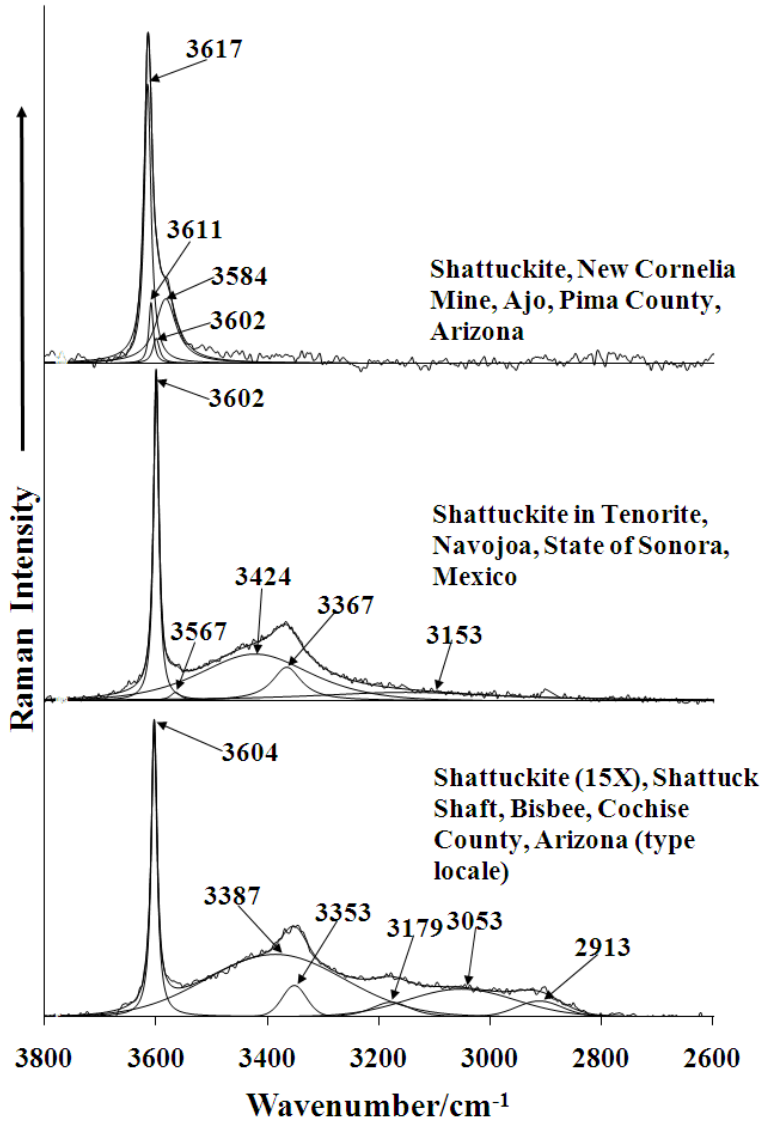

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280 **Figure 3**
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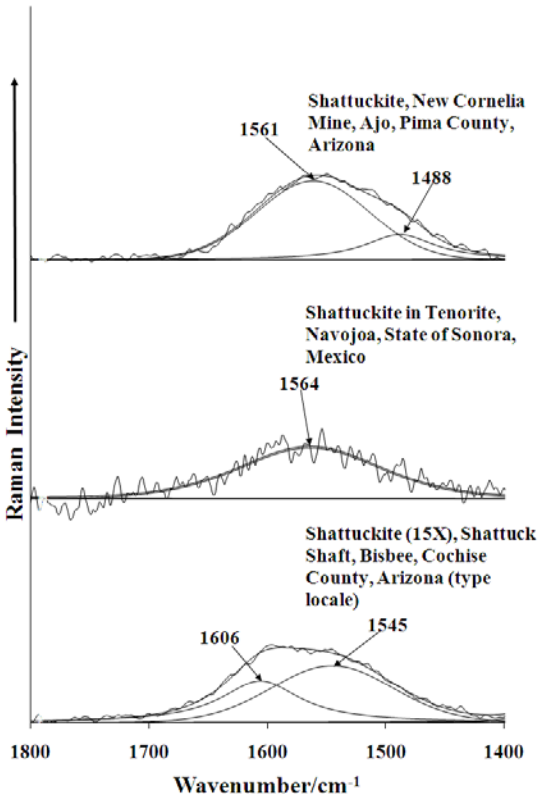

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285 **Figure 4**

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